Inorganica Chimica Acta, 52 (1981) 97–100

Voltammetric Behaviour of Transition Metal Complexes with Extended π System Schiff Base Ligands. N,N'-ethylenebis(monothioacetylacetoniminato)cobalt(II) and -palladium(II) Complexes

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Received March 4, 1981

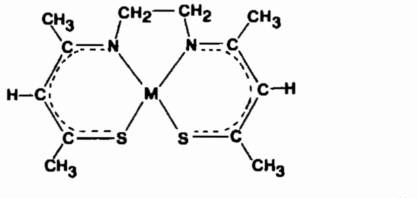
Redox properties of the complexes of Co(II) and Pd(II) with the extended π system N,N'-ethylenebis(monothioacetylacetoniminate) ligand are studied in acetonitrile solvent at platinum and mercury electrode by cyclic voltammetry and controlled potential coulometry. The Co(II) complex undergoes a reduction process giving rise to the corresponding Co(I) species, stable in the electrolysis solution; the oxidation product, [Co{(sacac)₂en}]⁺, stable in solid state, decomposes in solution phase.

The electroreduction of the Pd(II) complex occurs by two subsequent cathodic processes, originating the unstable species [Pd{(sacac)₂en}]⁻ and [Pd{(sacac)₂en}]²⁻. The anodic oxidation product is the species [Pd{(sacac)₂en}]²⁺, from which the starting complex can be electrolytically regenerated.

Introduction

The π-electron delocalized system N,N'-ethylenebis(monothioacetylacetoniminate), $[(sacac)_2en]^{2-}$, is a tetradentate Schiff base able to form stable complexes with divalent metal ions of transition elements and to stabilize them in uncommon oxidation states [1, 2]. Furthermore, $[(sacac)_2en]^{2-}$ is the precursor of a series of ligands which give cobalt chelates able to bind reversibly with molecular oxygen [3].

In order to complete a systematic study on the redox properties of the complexes formed by this ligand with transition metal ions [1, 2, 4], we report here the voltammetric behaviour of $[Co\{(sacac)_2en\}]$ and $[Pd\{(sacac)_2en\}]$ (1) in acetonitrile solvent.



(1)

Cyclic voltammetry and controlled potential coulometry were employed as main electroanalytical techniques.

Experimental

The $[Co\{(sacac)_2en\}]$ complex was prepared, purified and characterized as described in the literature [5]; in the synthesis of $[Pd\{(sacac)_2en\}]$ anhydrous $PdCl_2$ was previously converted into the corresponding acetonitrile solvate by refluxing its acetonitrile (MeCN) solution for two hours; from the crystallized product the Pd(II) complex was obtained by the same procedures used for the nickel and copper complexes [5].

Owing to the high reactivity of the cobalt complex solutions with oxygen, all the experiments were performed on solutions carefully deaerated by bubbling ultrapure argon.

All the chemicals and reagents, as well as the employed apparatus and experimental conditions, were already described [1, 2]. Unless otherwise specified, all the potential values are referred to an aqueous saturated calomel electrode.

To eliminate the effect of variable diffusion potentials at the aqueous–nonaqueous interface, the $E_{1/2}$ values of the studied redox couples, whenever possible, are referred to the $E_{1/2}$ of ferricinium/ferrocene couple, evaluated by voltammetric tests under the same experimental conditions.

Results and Discussion

[Co{(sacac)₂en}]

Figure 1 reports the cyclic voltammetric curves recorded at platinum electrode on a $[Co\{(sacac)_2en\}]$, MeCN solution, with 0.1 *M* tetraethylammonium perchlorate (TEAP) as supporting electrolyte. In the cathodic scan a single reduction process is evidentiated; coulometric tests carried out at about −1.70 V revealed the one-electron character of this

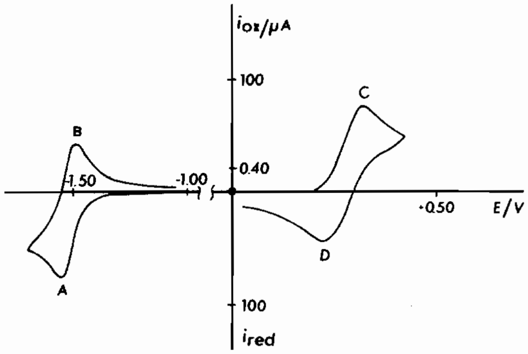


Fig. 1. Cyclic voltammetric curves relative to a 4.5×10^{-3} *M* [Co{(sacac)$_2$en}], 0.1 *M* TEAP, acetonitrile solution. Platinum working microelectrode; scan rate 0.2 Vs^{-1}. ● starting potential for both cathodic and anodic scans.

process. From cyclic voltammograms carried out at potential scan rates, v, ranging from 0.05 to 100 Vs^{-1} it could be deduced that an uncomplicated reversible electrode process is involved in the A–B peak system; in fact, the $(E_p)_A$ value was constant and equal to −1.54 V, the quantity $(E_p)_B - (E_p)_A$ was always equal to 58 ± 3 mV, the difference $(E_{p/2})_A - (E_p)_A$ resulted of 57 ± 3 mV, the $(i_p)_A/v^{1/2}$ parameter remained unchanged at varying v, as well as the ratio $(i_p)_B/(i_p)_A$, always equal to 1. The same results were obtained by using a mercury microelectrode which, indeed, did not allow to evidentiate any further reduction process.

During the electrolysis at −1.70 V the solution, initially red-brown in colour, turned to deep green; the formed species proved to be extremely air-sensitive, so that spectrophotometric analyses of the solution had to be performed using a spectroelectrochemical cell; a drawing of this cell is reported in Fig. 2. The visible spectrum obtained showed an absorption band with a λ_{max} of 695 nm; at higher frequencies more intense absorptions appeared. This spectrum is similar in shape to that exhibited by MeCN solutions of [Ni{(sacac)$_2$en}] in the same conditions, the λ_{max} being of 602 nm in this case.

As the Ni(II) complex shows substantially a square planar geometry both in the solid state and in solution phase [5, 7, 8], the comparison between the two spectra allows us to suggest that the reduction product is a cobalt(I) complex with a square planar stereochemistry. This type of geometry is also typical for the parent cobalt(II) complex [8]; the reversible character of the charge transfer process agrees well with similar conclusions. The absorption at 695 nm could be attributed to d–d transitions, on the basis of the assignment for similar square planar Schiff base Ni(II) complexes with sulphur donor atoms [9, 10].

Cyclic voltammograms recorded on the electrolyzed solution showed that only the reduced form of the redox couple responsible for the A–B peak system was present; any attempt to recover it failed, because of its high reducing power. By anodic reoxidation the starting compound was again obtained.

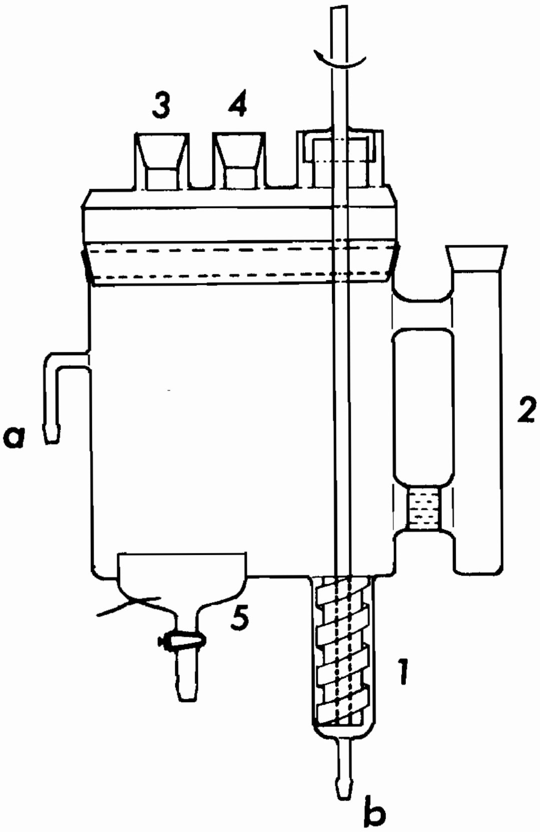


Fig. 2. Spectroelectrochemical cell. (1) Motor-driven Archimedes' screw; (2) auxiliary electrode; (3) inlet for reference electrode; (4) inlet for platinum working electrode; (5) mercury pool working electrode; a) to the cuvette; b) from the cuvette. Argon inlet and outlet are omitted for clarity.

An $E_{1/2}$ value of −1.88 V *vs.* ferricinium/ferrocene has been evaluated for the redox couple [Co{(sacac)$_2$en}]/[Co{(sacac)$_2$en}]$^-$.

All these findings agree well with Schrauzer's theory on metal complexes with 'odd–even ligands' [11]; they are also in agreement with the results obtained in electrochemical studies on the complexes [Ni{(sacac)$_2$en}] and [Cu{(sacac)$_2$en}] [1, 2].

In Fig. 1 the occurrence of an anodic process is also shown; coulometric tests led to a consumption of one mole of electrons per mole of starting compound. A dark precipitate formed during the electrolysis; cyclic voltammetric tests performed at the end of these experiments showed that the oxidized form of the redox couple responsible for the C–D peak system was present in the solution in an amount much lower than that of the parent compound

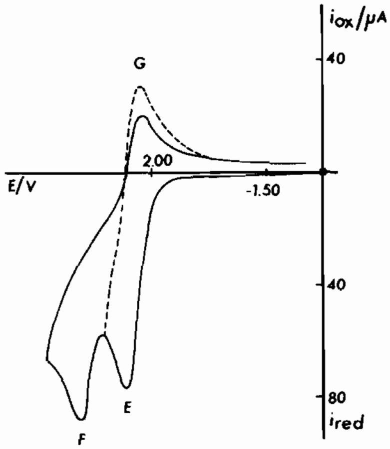


Fig. 3. Cyclic voltammetric curves recorded on a 3.30×10^{-3} *M* [Pd{(sacac)$_2$en}], 0.1 *M* TEAP, acetonitrile solution. Mercury working microelectrode; scan rate 0.2 Vs^{-1}.

initially present. The precipitate was recovered by filtration and washed with MeCN; i.r. spectra performed by using KBr pellet technique showed absorption bands typical of uncoordinated ClO_4^- ions (1110 and 625 cm^{-1}), together with the bands proper for the parent compound, shifted towards lower wavenumbers, according to the increased positive charge of the complex. The quantitative determination of cobalt content carried out by atomic absorption technique, and of chloride ion, performed according to Schöniger's method [12], indicated a Co:Cl molar ratio of about 1:1. Other analytical measurements, such as ^{1}H n.m.r. and conductivity tests, were prevented both by the low solubility of the compound in different solvents and by its fast decomposition in solution phase.

The whole of voltammetric and coulometric data, together with those obtained from infrared spectra and elemental analysis, are in agreement with the hypothesis that the oxidation product is the species [Co{(sacac)$_2$en}] [ClO_4].

Cyclic voltammetric tests at different potential scan rates revealed the quasi-reversible character of the charge transfer involved in the peak system C–D. The kinetic parameters of this charge transfer have been drawn out by comparison between experimental and theoretical responses computed by means of the digital simulation technique [13] at potential scan rates of 0.2, 1.0 and 10.0 Vs^{-1}. A charge transfer coefficient (α) of 0.5 and a standard heterogeneous rate kinetic constant ($k_{s,h}$) of 3.51×10^{-3} cm s^{-1} were evaluated.

An $E_{1/2}$ value of -0.295 V *vs.* ferricinium/ferrocene was calculated for the redox couple [Co{(sacac)$_2$en}]$^+$/[Co{(sacac)$_2$en}].

[Pd{(sacac)$_2$en}]

Figure 3 shows the cathodic portion of a cyclic voltammogram recorded at a mercury electrode on a [Pd{(sacac)$_2$en}], MeCN solution, with 0.1 *M* TEAP as supporting electrolyte. Two subsequent reduction processes occur at very negative potential values. Cyclic voltammetric experiments at different potential scan rates on the E–G catho–anodic peak system revealed that the cathodic peak potential was constant and equal to -2.11 V; all the parameters of the response were typical of an uncomplicated one-electron charge transfer.

An $E_{1/2}$ value of -2.08 V can be attributed to the redox couple [Pd{(sacac)$_2$en}]/[Pd{(sacac)$_2$en}]$^-$.

The second cathodic process occurs at potentials only slightly more negative than those of the first one. No directly associated anodic peak could be recorded, even at the highest explored scan rates; at low scan rates the $(i_p)_F/(i_p)_E$ ratio resulted lower than unity. At increasing scan rate $(E_p)_F$ shifted towards negative values and at $v > 10$ Vs^{-1} the peak separation was high enough so that the $(i_p)_F/(i_p)_E$ ratio assumed a value near to one.

The whole of the voltammetric trend agrees with the occurrence of a two-step charge transfer process consisting of a first reversible one-electron step followed by a totally irreversible one-electron charge transfer [14]. The fact that the anodic peak directly associated to the less cathodic one is still well detectable also by switching the potential scan after traversing the second cathodic peak can be explained assuming that the E^0 value of the redox couple [Pd{(sacac)$_2$en}]$^-$/[Pd{(sacac)$_2$en}]$^{2-}$ is more negative than that of the couple [Pd{(sacac)$_2$en}]/[Pd{(sacac)$_2$en}]$^-$. It follows that the reduced species arising at the second cathodic peak reacts fast with the parent compound, generating the species [Pd{(sacac)$_2$en}]$^-$.

In the controlled potential coulometric experiments carried out both at potentials corresponding to the foot of the first peak and directly at the second one the electrolysis current did not reach the values of the background current after consuming either one or two electrons per depolarizer molecule. It is likely that the anionic complexes produced in the reduction processes decompose, generating species reducible in their turn in that potential region.

The complex [Pd{(sacac)$_2$en}] undergoes an oxidation process as shown by the appearance of an anodic peak ($E_p = +0.8$ V) in cyclic voltammograms recorded with a platinum working electrode. Controlled potential coulometric tests allowed to state that two electrons per molecule are involved in the overall oxidation process. Unfortunately the voltammetric tests led to poorly reproducible responses, strongly dependent on the electrode 'history', both with regard to the peak height and to its shape. A cathodic peak directly associated to the anodic one was sometimes detectable; the ratio between cathodic and anodic peak currents increased at increasing scan rate. This fact allows to hypothesize the occurrence of an e.c.e. type mechanism.

Cyclic voltammetric tests on the exhaustively electrolyzed solution showed a cathodic peak ($E_p \cong -0.25$ V at $v = 0.2$ Vs^{-1}) with features typical of an irreversible charge transfer process; by electrolysis in correspondence to the reduction potentials the starting compound was regenerated with a yield of about 50%.

The coulometric data together with the i.r. spectra and conductivity tests performed on the recovered oxidized complex allowed to state that the oxidation product is a two-charged cationic species with structural features not significantly different from those of the parent compound. Hence the different $[M\{(sacac)_2en\}]$ complexes studied [M = Ni, Cu, Co, Pd] lead to four different stable anodic oxidation products: in the case of the nickel complex the species $[Ni\{(sacac)_2en\}]^{4+}$ forms [11], no stable cationic copper complex can be obtained [2], cobalt and palladium complexes give $[Co\{(sacac)_2en\}]^+$ and $[Pd\{(sacac)_2en\}]^{2+}$, respectively.

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